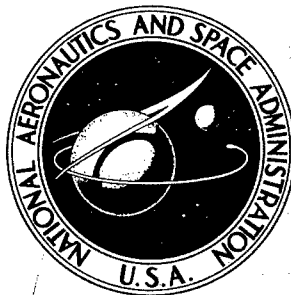


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by I. N. Frantsevich and I. I. Koven'skiy

From *Dopovidi Akademii Nauk Ukrain's'koi RSR*,
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Translation of "Pro stan vugletsyu v titani, tantali ta vol'frami"

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THE STATE OF CARBON IN TITANIUM, TANTALUM AND TUNGSTEN

I. N. Frantsevich and I. I. Kovens'kiy

ABSTRACT

T: FRA
The authors investigated carbon electrotransport in titanium, tantalum and tungsten, the carbon content being 0.1 percent by weight. The experimental data were used to determine the charges of the carbon ions in the given metals.

A number of properties of metal alloys are determined by the nature of interaction of their atoms. In the theory of heat resistance, the strength of the interatomic bond in solid metal solutions is regarded as one of the basic factors determining the behavior of alloys at high temperatures. The development of the heat-resistant properties is connected with the rational selection of the basic metal and the component elements. The stabilizing role of certain alloying admixtures in solid metal solutions is, in some measure, determined by the extent to which their atoms are capable of releasing their electrons for the restoration of the d-sublevels in the basic metal. This problem is very important because the heat-resistant alloys, as a rule, consist of metals which are classified as transitional elements. It is clear, therefore, that the establishment of the state of the atoms in the components of solid solutions is a matter of great importance.

An effective method in this connection is the investigation into the electrotransport, that is the ion migration set off under the overall effect of the electric field force applied to the alloy and the force generated by the interaction between the electron ions and the p-type conductivity (the so-called electron hole flux). If the ions are predominant in their interaction with the electrons in the alloy under investigation, the resulting force flows to the anode; otherwise, it is directed to the cathode. Thus, the effect of the electrotransport whose magnitude is related to the diffusive mobility of the atoms is actually determined by the same type of interaction of the electrons and holes with the ions. A study of the electrotransfer is therefore very important for the establishment of the interrelation between the two processes: diffusion and electric conductivity.

The following equation has evolved from the recently-developed electrotransport theory (1, 2):

$$Z^* = z - n_1 \sigma_1 l_1 + n_2 \sigma_2 l_2, \quad (1)$$

where z represents the ion charge; n_1 , σ_1 , l_1 and n_2 , σ_2 , l_2 are the density, the scattering cross section of the migrating ions and the respective free-path lengths of the electrons and hole conductivity; Z^* is some effective charge that includes both the interaction between the ion and the field and the force of the electron hole flux. The Z^* value can be calculated by the use of the Einstein formula (3) and by taking into account the correlation factor between the successive shifts of the migrating ion f (4):

$$Z^* e D = B k T f, \quad (2)$$

where e represents an elementary charge; D is the diffusion factor at absolute temperature in experiment T ; B is the ion mobility in the field in v/cm ; k is the Boltzmann constant.

The definition of z , which is very important, is made possible by an investigation into the electrotransport within a sufficiently wide temperature range. If the latter is characterized by the correlation $\rho = \rho_0 + \alpha T$ where ρ is the electric resistance of the alloy, and α its

temperature coefficient, then if $\frac{\rho_0}{\alpha} = \frac{\rho_{0-}}{\alpha_-} = \frac{\rho_{0+}}{\alpha_+}$ (here ρ_{0-} , α_- , ρ_{0+} , α_+ are the same values as ρ_0 and α but such that characterize the electron and hole conductivity), the dependence of Z^* on $x = \frac{1}{T + \frac{\rho_0}{\alpha}}$ can be expressed by a straight line equation (5)

$$Z^* = z + a \frac{1}{T + \frac{\rho_0}{\alpha}}. \quad (3)$$

But in case $\frac{\rho_0}{\alpha} \neq \frac{\rho_{0-}}{\alpha_-} \neq \frac{\rho_{0+}}{\alpha_+}$, the mentioned dependence can be described by the following hyperbolic equation (6):

$$Ax^2 + BxZ^* - Cx - Z^* + z = 0. \quad (4)$$

The A , B and C parameters include the values characterizing the scattering of the electrons and hole conductivity by the migrating ions as well as the temperature level of the electric conductivity.

The formulas of the two-zone metal model were used for writing equations (3) and (4).

[This article deals with an investigation of carbon electrotransport in titanium, tantalum and tungsten (the carbon content being about 0.1 percent by weight). The experiments involved the use of a C^{14} radioactive isotope.]

The carbon diffusion factors included in correlation (2) were determined on the same models which were used for the study of the electrotransport. This was necessary in order to enhance the accuracy of the calculations as the D values, defined by the different authors for the same metal, may differ a great deal from each other (see (7), for example).

[The models consisted of pieces of wire made of the mentioned alloy and measuring about 0.6 mm in diameter and 70 mm in length. In the middle of the models was a clearly outlined zone marked with a C^{14} radioisotope. That zone was made sufficiently wide, and the equation of the diffusion from an infinite source (8) was used to calculate the diffusion coefficients.]

The models were heated in a protective atmosphere by a direct current. The latter produced an electric field and heated the models to the desired temperature which was controlled by a KhGIMIP-type optical pyrometer.

Before and after heating it on a "B" installation, the distribution of radioactivity on the model was measured on every other 0.1 mm segment. Inasmuch as the radioactivity is proportional to the carbon concentration, the measurements revealed the distribution of the carbon in relative values along the length of the model. The carbon diffusion coefficients were calculated on the basis of the concentration curve, and the speed of its electrotransport at all temperatures by the displacement of the radioactive zone.

The experiments involved in the study of carbon electrotransport in titanium were carried out at 950, 1000, 1050, 1150, 1250, 1350, 1450, 1550 and 1650°C in tantalum at 600,¹ 800, 1000, 1200, 1400, 1800, 2200 and 2600°C; in tungsten at 1800, 1850 and 1900-2800°C every 100°.

[The resulting diffusion coefficients were used for calculating the activation energy magnitudes and the pre-exponential factors for all the solutions shown in Table 1.] In the case of a Ta-C alloy, these magnitudes

¹ The models were heated in an oven at this temperature. A thermocouple was used in place of a pyrometer.

were calculated within the range of 600-1400°C inasmuch as higher temperatures revealed a deviation from the usual exponential dependence of the diffusion factors toward an increase. The latter were found to be equal to $9.54 \cdot 10^{-6}$; $3.01 \cdot 10^{-5}$; $6.58 \cdot 10^{-5}$ cm²/sec. at 1800, 2200, and 2600°C respectively.

(Table 1

Alloy	D_0 cm ² /sec.	E , cal/g-atom
Ti - C	3.18×10^{-3}	18,900
Ta - C	2.78×10^{-3}	24,600
W - C	9.22×10^{-3}	40,400

The experimental data made it possible to define the effective Z^* charges, and the method of least squares was used to calculate the parameters of equations (3) and (4). The latter are cited in Table 2:

Alloy	$\frac{\rho_0}{\alpha}$, degrees	$B \cdot 10^{-3}$, degrees	$C \cdot 10^{-3}$, el.unit.x deg.	z , el.unit	a , el.unit.x deg.
Ti - C	1,748	2,850	7,597	4.0	-
Ta - C	88	-	-	2.8	25,480
W - C	15	1,969	-0,196	0.6	-

It has been established that the carbon charges in titanium and tungsten are governed by the temperature dependence which is described by equation (4). In the case of a tantalum-carbon alloy, the effective charges of the latter satisfy a straight line equation. Parameter A of equation (4) for both alloys--titanium-carbon and tungsten-carbon--was found to be so small that the magnitude of the first term of this equation could be ignored.

In all the three alloys the carbon in the process of electrotransport shifted toward the cathode. The magnitude of the effective charges always exceeded z . This indicates that the hole migration plays an essential part in the transport of carbon in the mentioned metals.

Table 2 shows that the carbon dissolved in the titanium-tantalum-tungsten series diminishes in quantity.

The energy required to produce the total electron charge in the metal and metalloid is determined by the correlation between the energy released by the metalloid electron filling of the vacancies on the d-sublevels and the ionization energy of the metalloid atom. In the case of tungsten which has a high energy of 5d-sublevels, the transport of metalloid electrons to these levels is accompanied by heat absorption, whereas in the case of titanium and tantalum the low d-sublevels are apparently filled by the filling energy passing above the ionization energy (9), which explains the sharp decrease in the carbon content in tungsten as compared to its charge in titanium and tantalum. In the latter two metals, the decrease in the carbon content is apparently due to a larger extent of d-sublevel filling in tantalum as compared to titanium.

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